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A Ferracarborane Analogue to $[Fp]^-$. Synthesis and Reactions of $[closo\text{-}3,3\text{-}(CO)_2\text{-}3,1,2\text{-}FeC_2B_9H_{11}]^{2-}$

by
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Reduction of [*closo*-3,3,3-$(CO)_3$-3,1,2-$FeC_2B_9H_{11}$] (1) with 2 equiv of sodium naphthalide affords the high-yield synthesis of a formal iron(0) ferracarborane dianion [*closo*-3,3-$(CO)_2$-3,1,2-$FeC_2B_9H_{11}]^{2-}$ (3), as monitored by ^{11}B NMR spectroscopy. Complex 3 serves as a nucleophile in a variety of alkylation, acylation, and metalation reactions to yield ferracarborane anions of the type [*closo*-3,3-$(CO)_2$-3-L-3,1,2-$FeC_2B_9H_{11}]^-$ (4, L = CH_3; 5, L = $CH_2C_6H_5$; 6, L = $COCH_3$; 7, L = SnC_6H_5). The molecular structure of $[N(C_2H_5)_4][7]$ has been determined by X-ray diffraction techniques. Compound 7 crystallized in the triclinic space group $P\bar{1}$ with a = 11.209 (1) Å, b = 13.026 (1) Å, c = 13.595 (1) Å, α = 79.959 (3)°, β = 84.143 (3)°, γ = 66.060 (2)°, V = 1785 Å^3, and Z = 2. *In situ* reactions of 3 with allyl and methylallyl chloride followed by subsequent loss of CO induced by ultraviolet radiation, resulted in the isolation of the corresponding η^3-allyl derivatives, [*closo*-3-CO-3-(η^3-CH_2CRCH_2)-3,1,2-$FeC_2B_9H_{11}]^-$ (8, R = H; 9, R = CH_3). The structure of 8 as the PPN^+ salt was also elucidated by single-crystal X-ray diffraction and found to crystallize in the monoclinic space group $P2_1/m$ with a = 9.1250 (7) Å, b = 25.011 (2) Å, c = 18.517 (2) Å, β = 91.328 (3)°, V = 4225 Å^3, and Z = 4 (two crystallographically different half-anions and one cation in the asymmetric unit). Migratory

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19. Abstract (cont.)

insertion of alkyls was demonstrated in the preparation of [*closo*-3-CO-3-$COCH_3$-3-$P(CH_3)_3$-3,1,2-$FeC_2B_9H_{11}$]$^-$ (**10**) by heating **4** and excess $P(CH_3)_3$ in THF for 7 days at the reflux temperature. A single-crystal X-ray diffraction study of [PPN][**10**] is reported. Complex **10** crystallized in the triclinic space group $P\bar{1}$ with a = 10.086 (4) Å, b = 15.390 (6) Å, c = 17.027 (7) Å, α = 112.636 (8)°, β = 96.647 (8)°, γ = 100.206 (9)°, V = 2351 Å^3, and Z = 2. The closo 12-vertex icosahedral geometry composed of a polyhedral FeC_2B_9-d_6 framework and pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all three of the ferracarboranes that were characterized crystallographically.

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